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(54) Title: DRY CLEANING COMPOSITIONS AND THEIR USE

(57) Abstract: A dry cleaning composition comprising: (a) more than 60 wt % to 99.9 wt % of an Isoparaffinic solvent having a molecular average of at least 9 carbon atoms; (b) from 0.01 wt % to 39 wt % of water; (c) from 0.01 wt % to 39 wt % of emulsifier; and (d) from 0.001 wt % to 39 wt % of a cleaning auxiliary.

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DRY CLEANING COMPOSITIONS AND THEIR USE

Technical Field

The present invention relates to dry cleaning compositions
5 based on organic solvents and processes.

Background of the Invention

Traditionally, dry cleaning processes are carried-out using organic solvents, in particular, perchloroethylene (PERC).

10 Stains are first removed by hand, typically using soap and/or surfactant, in a process known as "pre-spotting".

Recently, health and safety concerns surrounding PERC have lead to a search for alternative systems. For example, US-A-5 419 849 and US-A-5 454 969 disclose cleaning fluids for fabrics
15 based on one or more hydrochlorofluorocarbons and/or hydrofluorocarbons, one or more alcohols and/or glycol ethers and one or more paraffinic hydrocarbons.

Another trend of recent times is to attempt to include in dry cleaning compositions, one or more auxiliary cleaning agents
20 such as of the type used in conventional laundry wash products.

This has been achieved for dry cleaning systems which utilise liquid carbon dioxide instead of organic solvents. There, surfactant and water are used to create reverse micelles, e.g. as described in US-A-5 158 704 and US-A-5 266 205.

25 It is known to deliver hydrophilic fluoescers (a common laundry wash ingredient) in dry cleaning processes of the organic solvent type. US-A-3 640 881 describes how a hydrophilic fluoescer pre-mixed with water can be incorporated in a perchlorethylene (PERC) dry cleaning bath.

US-A-4 438 009 discloses a pre-spotting composition for use before dry cleaning, in which 1-30% of salts such as sodium citrate are included in a liquid comprising 5-60% of
5 hydrocarbon solvent such as limonene or an isoparaffin, 1-35% of nonionic surfactant and 40-75% of water.

We have now discovered that larger amounts of isoparaffinic solvents can be used to incorporate a wider range of cleaning auxiliaries and with greater efficacy.

10 Definition of the Invention

Thus, the present invention now provides dry cleaning composition comprising:

- 15 (a) more than 60wt% to 99.9wt% of an isoparaffinic solvent having a molecular average of at least 9 carbon atoms, preferably from 70wt% to 99wt%, more preferably from 80wt% to 99wt%;
- (b) from 0.01wt% to 39wt% of water, preferably from 0.05wt% to 29wt%, more preferably from 0.1wt% to 19wt%;
- 20 (c) from 0.01wt% to 39wt% of emulsifier, preferably from 0.05wt% to 29wt%, more preferably from 0.1wt% to 19wt%; and
- (d) from 0.001wt% to 39wt% of a cleaning auxiliary, preferably from 0.01wt% to 29wt%, more preferably
25 from 0.03wt% to 19wt%.

Detailed Description of the Invention

The Isoparaffinic Solvent

As used herein, the term "isoparaffinic solvent" means one or 5 more branched alkanes having on average, at least 9 carbon atoms, preferably from 10 to 16 carbon atoms.

Suitable isoparaffinic solvents, include those sold as DF-2000 or Isopar L, namely a mixture of C₁₁ to C₁₅ alkanes ex Exxon 10 Mobil. These isoparaffinic solvents are branched chain fully saturated hydrocarbons and are characterised by boiling range.

These mixtures are available in boiling ranges from 180°C to 210°C. In addition to the isoparaffinic hydrocarbons, low odor petroleum solvent having a boiling range of 195°C to 250°C, 15 kerosene and d-Limonene also are acceptable. From an odor standpoint, the isoparaffinic solvents are preferred, as these materials are low odor. However, if odor is not a consideration, substantially any of the above solvents can be utilised.

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The Emulsifier

The compositions of the present invention also include an emulsifier, for example one or more surfactants selected from anionic, nonionic, cationic, zwitterionic and amphoteric 25 surfactants. One preferred selection comprises those disclosed in US-A-4 438 009. The first component of such a suitable nonionic surfactant mixture may be a sorbitan surfactant, such as sorbitan monolaurate, sorbitan mono-oleate, sorbitan

trioleate and mixtures thereof. The second component of the nonionic mixture includes the following classes of nonionic surfactants: the ethoxylated nonylphenols, such as the Surfonic N Series available from Jefferson Chemical the ethoxylated 5 octylphenols, including the Triton X Series available from Rohm & Haas, the ethoxylated secondary alcohols, such as ³/₄ Tergitol Series available from Union Carbide, the ethoxylated primary alcohol series, such as the Neodols available from Shell Chemical, the polymeric ethylene oxides, such as the Pluronics 10 available from B.A.S.F. Wyandotte, and the ethylene oxide propylene oxide block copolymers, such as the Plurafacs available from B.A.S.F. Wyandotte.

The preferred nonionic surfactants recited in US-A-4 438 009 15 are the ethoxylated nonylphenols and the ethoxylated octylphenols, as these materials have excellent oil and water dispersibility, good detergency characteristics and can produce stable oil-out emulsions. The particularly preferred surfactants are nonylphenols having from 2 to 8 moles of 20 ethylene oxide, and particularly, nonylphenol having 6 moles of ethylene oxide combined with a small amount of nonylphenol reacted with 2 moles of ethylene oxide.

As an additional nonionic surfacant, it is often desirable to 25 incorporate an amount of an ethoxylated sorbitan nonionic, such as those sold under the tradename Tweens. Suitable nonionics include ethoxylated sorbitan monolaurate plus 20 moles ethylene oxide, ethoxylated sorbitan monopalmitate with 20 moles or less of ethylene oxide, ethoxylated sorbitan monostearate with 20 30 moles or less of ethylene oxide, ethoxylated sorbitan

monooleate with 20 moles or less of ethylene oxide and mixtures thereof. The Tween-type ethoxylated sorbitan nonionics, when combined with the non-ethoxylated sorbitan nonionics in appropriate amounts, provide excellent emulsion stability, increased stain removal performance and improved inhibition of soil redeposition.

In the most general sense, however, the emulsifier is chosen from one or more of soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic surface-active compounds and mixtures thereof. Many suitable surface-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Such surfactant(s) may be selected from one or more soaps and synthetic non-soap anionic and non-ionic compounds.

For example, the compositions of the invention may contain linear alkylbenzene sulphonate anionic surfactants, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅.

The compositions of the invention may additionally or alternatively contain one or more other anionic surfactants. Suitable anionic surfactants are well-known to those skilled in the art. These include primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-
5 C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

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It is often preferred if the level of total non-ionic surfactant is less than the total amount of anionic surfactant (if present).

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Another class of suitable surfactants comprises certain mono-long chain-alkyl cationic surfactants. Cationic surfactants of this type include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are long or short
20 hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R₁ is a C₈-C₂₂ alkyl group, preferably a C₈-C₁₀ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄, which may be the same or different, are methyl or hydroxyethyl
25 groups); and cationic esters (for example, choline esters).

The Cleaning Auxiliary

Suitable cleaning auxiliaries may be selected from any one or
30 more of those included in conventional laundry wash compositions, e.g. selected from detergency builders, bleaches, alkaline agents, fluorescers and mixtures thereof.

Detergency Builders

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever³); crystalline and amorphous aluminosilicates³, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

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Another suitable class of builders comprises the alkali metal, preferably sodium, aluminosilicates.

20 The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:
 $0.8-1.5 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8-6 \text{ SiO}_2$.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium

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aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

- The zeolite may be the commercially available zeolite 4A now
5 widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal
10 aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.
- 15 Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.
- 20 Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethyloxy succinates,
25 carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.
- 30 Especially preferred organic builders are citrates and acrylic polymers, more especially acrylic/maleic copolymers.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Bleaches

- 5 Compositions according to the invention may also suitably contain ^aa bleach system. Fabric washing compositions ^amay desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.
- 10 Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate
- 15 monohydrate and tetrahydrate, and sodium percarbonate.
- Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and
- 20 sodium silicate is disclosed in GB 2 123 044B (Kao).
- The peroxy bleach compound is suitably present in an amount in excess of that of the bleach precursor.
- 25 Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pernoanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are N,N,N',N',-tetracetyl ethylenediamine (TAED) and sodium
- 30 noanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A

(Unilever), and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) are also of interest.

The bleach system can be either supplemented with or replaced by
5 a peroxyacid. examples of such peracids can be found in US 4 686 063 and ³US 5 397 501 (Unilever). A preferred example ⁴is the imido peroxy²carboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phtalimido peroxy caproic acid (PAP).

10

A bleach stabiliser (transistor metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as ED³DS
15 (ethylene diamine di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.

20 An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

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Enzymes

Compositions according to the invention may also contain one or more enzyme(s). Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable
30 for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis

reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and
5 origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of B. Subtilis B. licheniformis, such as the commercially available subtilisins
10 Maxatase (Trade Mark), as supplied by Gist Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of
15 Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases
20 are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).

25 Fluorescers

Fluorescers may also be included, either hydrophobic and/or hydrophotic types.

Some preferred classes of hydrophobic fluorescers are coumarins, eg Tinopal SWN and bis-benzoxazoles, eg. Tinopal SOP.

30 Some preferred classes of hydrophilic fluorescers are those which are organic fluorescers having one or more hydrophilic groups independently selected from sulphonate, carboxylate,

sulphate, phosphate, phosphonate, phosphinate, hydroxyl, (primary, secondary and tertiary)amino and (poly)alkoxylated groups. Some preferred types include water-soluble and water-dispersible distyrylbiphenyl derivatives, distilbene derivatives, especially cyanuric chloride/diaminostilbene derivatives and dibenzofuranbiphenyl derivatives.

Alkaline Agents

Suitable alkaline agents include alkali metal carbonates, silicates and metasilicates, alone or in combination.

10 The present invention will now be explained in more detail by way of the following non-limiting examples.

Example 1

Component	weight%	Detergent product	weight%
Isopar L	97	Na-citrate	25
Water	1.0	Sokalan CP45	3.3
Aerosol OT	0.67	TAED	14
Plurafac LF403	1.0	Na-percarbonate	41
20 Detergent product	0.11	Dequest 2047	2.0
		Light soda ash	8.4
		Na-CMC	1.1
		Tinopal CBS-X	3.4
		Savinase	2.1
25			
Total	100	Total	100

Experimental procedure

This procedure describes the cleaning of oil (dirty motor oil, kitchen grease, spaghetti sauce), particulates (sebum, soot, clay) and bleachable (tea) stain monitors. In this example the
5 total monitor weight was 10.3 g and the liquid to cloth ratio was 13 g/g, requiring 134 g of emulsion fluid. Therefore, 0.90 g AOT and 1.34 g Plurafac LF403 were dissolved in 130 g DF-2000, and 0.15 g detergent product was dissolved in 1.34 g of water. Mixing both solutions together formed the emulsion.
10 The cleaning took place in a rotating closed container including both the emulsion and the stain monitors. Similarly, an identical set of monitors was washed with a traditional laundry detergent (5 g/L) and water.

15 Results

The emulsion showed excellent cleaning compared to cleaning with water and a traditional laundry detergent. Additionally, the emulsion resulted in very good fabric care compared to traditional water-based cleaning.

Claims

1. A dry cleaning composition comprising:
 - (a) more than 60wt% to 99.9wt% of an isoparaffinic solvent having a molecular average of at least 9 carbon atoms, preferably from 70wt% to 99wt%, more preferably from 80wt% to 98wt%;
 - (b) from 0.01wt% to 39wt% of water, preferably from 0.05wt% to 29wt%, more preferably from 0.1wt% to 19wt%;
 - (c) from 0.01wt% to 39wt% of emulsifier, preferably from 0.05wt% to 29wt%, more preferably from 0.1wt% to 19wt%; and
 - (d) from 0.001wt% to 39wt% of a cleaning auxiliary, preferably from 0.01wt% to 29wt%, more preferably from 0.03wt% to 19wt%.
2. A composition according to claim 1, when the isoparaffinic solvent has an average of from 10 to 16 carbon atoms, preferably from 11 to 15 carbon atoms.
3. A composition according to either preceding claim, wherein the emulsifier comprises one or more surfactants selected from ionic and nonionic surfactants and has an HLB of from 5 to 15.
4. A composition according to any preceding claim, wherein the weight ratio of water to emulsifier is from 20:1 to 1:20.
5. A composition according to any preceding claim, wherein the cleaning auxiliary is selected from detergency

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builders, bleaches, alkaline agents, fluoresceors, enzymes and mixtures thereof.

6. A process for dry cleaning textile fabrics, the process comprising contacting said fabrics with a composition according to any preceding claim, at atmospheric pressure and at ambient temperature.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06L1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	GB 2 238 793 A (KREUSSLER CHEM FAB) 12 June 1991 (1991-06-12) abstract; example 1 ---	1-6
A	US 5 419 849 A (FIELDS PAUL B ET AL) 30 May 1995 (1995-05-30) cited in the application example 2 ---	1,2,6
A	US 5 604 196 A (WELTMAN HENRY J ET AL) 18 February 1997 (1997-02-18) column 5, line 65 -column 6, line 6; table VII --- -/--	1,2,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 199512 Derwent Publications Ltd., London, GB; Class E19, AN 1995-085724 XP002169368 & JP 07 011298 A (SANKEN KK), 13 January 1995 (1995-01-13) abstract -----	1-3,6

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